

PATENT SPECIFICATION

1.159.689



DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Butadiene-Styrene-Methyl Methacrylate Cross-Linked Copolymers

We, KUREHA KAGAKU KOGYO KABUSHIKI KAISHA, a joint-stock Company of Japan, located at 8,1-chome, Nihonbashi Horidome-cho, Chuo-Ku, Tokyo-To, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 This invention relates to butadiene-styrene-methyl methacrylate cross-linked copolymers (hereinafter referred to as "MBS resins"). More particularly, the invention concerns a new MBS resin which, upon being mixed with a polyvinyl chloride or a copolymer having vinyl chloride as a principal constituent, is capable of imparting to the resulting shaped articles of the composition, high transparency, impact resistance, and resistance to stress-whitening occurring through bending.

10 So-called graft copolymers, produced by causing graft polymerization (consecutive polymerization hereinafter will be denoted merely as polymerization) of one or more vinyl or vinylidene monomers such as styrene, 25 acrylonitrile, or methyl methacrylate on a rubber-like polymer latex are already well known.

30 These graft copolymers have good mechanical strength and have, therefore, been used independently for various shaped articles. In addition, these graft copolymers have been mixed with other resins, such as polyvinyl chloride, to improve the impact resistance of shaped articles made from other resins.

35 Most of the graft copolymers produced by hitherto known methods, however, while being capable of improving the impact resistance of polyvinyl chloride when mixed and kneaded therewith, have been disadvantageous in that 40 [P- ...]

they produce products which are deficient in transparency and lack resistance to weathering. Furthermore, resin compositions having acrylonitrile as a constituent have such disadvantages as low heat stability.

45 In addition, when bends are formed in shaped articles, such as sheets and bottles, produced from these resins, the parts of the articles in the vicinity of these bends become extremely cloudy, giving products of low commercial value.

50 It is an object of the present invention to provide MBS resins which, upon being mixed and kneaded in minimal quantities with polyvinyl chloride are capable of imparting excellent properties such as high impact resistance, high transparency, resistance to weather effects, high heat stability and almost no occurrence of the stress whitening at bent parts of products formed from the resulting compositions.

55 Another object of the invention is to provide a relatively simple and economical process for producing MBS resins of the above stated character.

60 The present invention provides a process for producing a butadiene-styrene methyl methacrylate cross-linked copolymer in particulate form comprising from 24 to 60% by weight of butadiene from 22 to 43% by weight of styrene and from 5 to 46% by weight of methyl methacrylate, which comprises carrying out polymerization of styrene, methyl methacrylate and a cross-linking agent (the plastics component) in the presence of latex of polybutadiene or a butadiene-styrene copolymer (the rubber component), the styrene and methyl methacrylate in the plastics component comprising from 60 to 25% by weight and the butadiene and styrene (if any) in the 70 75 80



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rubber component comprising from 40 to 75% by weight, based on the total weight of butadiene, styrene and methyl methacrylate, and the cross linking agent comprising from 0.01 to 5% by weight, based on the total weight of butadiene, styrene and methyl methacrylate

In a preferred embodiment, the MBS resins according to the present invention are produced by a process wherein a first polymerisation mixture containing some or all of the styrene and some of the methyl methacrylate in the plastics component is polymerised with some of the cross linking agent in the presence of the polybutadiene or butadiene-styrene copolymer latex, and, in a second polymerisation step initiated after the first polymerisation step is complete, a second polymerisation mixture comprising the remainder of the methyl methacrylate and the remaining styrene (if any) is polymerised with the remainder of the cross-linking agent in the presence of the resulting latex, the first polymerisation mixture comprising more than 70%, by weight of the styrene and methyl methacrylate in the plastics component.

By mixing from 5 to 20 parts by weight of an MBS resin, obtained in this manner with from 95 to 80 parts by weight of polyvinyl chloride or vinyl chloride copolymer and forming shaped articles from the resulting resin, it is possible to produce products having the above-described excellent properties.

The particles of MBS resin produced by the processes described above have a layered structure with a core of polybutadiene or butadiene-styrene copolymer surrounded by a shell of a styrene-methyl methacrylate copolymer, and in a preferred embodiment, an outer shell largely comprising polymethyl methacrylate. When such particles are mixed and kneaded with vinyl polymers, the particles are dispersed through the vinyl chloride polymer, and show no tendency to separate therefrom since the methyl methacrylate in the shell has a high affinity for vinyl chloride polymers whilst the styrene has a high affinity for the rubber component. Moreover, since the particles are cross-linked the adhesion between the MBS particles is weak, so that these particles can be readily dispersed in a uniform manner. As a result, the transparency of the product is increased, and, at the same time, separation of the rubber layer and the polyvinyl chloride layer does not occur, so that stress whitening also does not occur.

An important feature of the present invention is that MBS resins obtained thereby are homogeneously dispersible in solvents such as benzene, toluene and tetrahydronaphthalene and that the reduced specific viscosity η_{sp}/c (4g./litre, benzene) thereof is within the range from 0.01 to 0.06. The reduced specific viscosity of an MBS resin obtained according to the invention decreases with an increase in

the degree of cross linking and increases with a decrease in the degree of cross linking.

It has been found that, while the mixing and kneading of polyvinyl chloride and an MBS resin having a value of η_{sp}/c lower than 0.01 results in a product with excellent transparency, the improvement in the impact resistance is small, and the product is not sufficiently tough unless at least 20% by weight of the MBS resin is added.

On the other hand, when the value of η_{sp}/c exceeds 0.06, the improvement in the impact resistance is increased, but particle dispersion becomes difficult, and a product of sufficient transparency cannot be obtained. Furthermore, the product is subject to a high degree of stress whitening.

Many of the MBS resins or ABS resins (butadiene-styrene-acrylonitrile copolymers) produced by heretofore known methods are insoluble in solvents such as benzene, and those which are soluble have reduced specific viscosities exceeding 0.1. These MBS resins and ABS resins have a further disadvantage in that shaped articles produced from mixtures of these resins with polyvinyl chloride do not have very good transparency.

Through consideration of these disadvantages features of the resins obtained by known methods, it has been discovered that there is a close interrelationship between the reduced specific viscosity and transparency as well as the stress whitening of MBS resins, as described more fully below.

A further feature of the present invention is that the refractive indices n_D^{20} of the MBS resins are within the range from 1.528 to 1.540. The refractive indices of polyvinyl chloride and copolymers with vinyl chloride as their principal constituent are from 1.530 to 1.538 at 20°C and it is important that the refractive indices of the MBS resins to be mixed with the polyvinyl chloride coincide almost exactly with these values. If the refractive index is outside the above-stated range, the resulting shaped article will be non-transparent or will, in some instances, produce scattered light of strong purple colour.

The refractive indices n_D^{20} at 20°C of homopolymers of butadiene, methyl methacrylate, and styrene at 1.515, 1.494, and 1.590, respectively, and because the refractive indices of the copolymers according to the invention are determined by the additive effects of the refractive indices of homopolymers of the constituent monomers, it is possible to provide copolymers having refractive indices similar to that of the polyvinyl chloride with which the copolymers are to be mixed.

The single figure of the accompanying drawing is a graphical representation, with triangular coordinates indicating the percentages by weight of three constituent monomers of MBS resins according to the invention. In the case where the entire composition of a

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resin is contained within the region bounded by the figure ABCDEF, and, at the same time, the resin possesses a value of η_{sp}/c within the above specified range, mixing and kneading of the resin with polyvinyl chloride produces a transparent shaped article. More specifically, it is essential that the amounts of the three monomers be from 24 to 60% by weight of butadiene, from 22 to 43% by weight of styrene, and from 5 to 46% by weight of methyl methacrylate.

A further important feature of the MBS resins according to the invention is the compositional ratio of the rubber component and the plastics component. Of course, if only impact resistance were to be considered as a problem, as large a rubber content as possible would be desirable, but if the rubber content is increased to an extreme degree, agglomeration or lumping will result from steps such as salting out and drying, or the mixing and kneading with the polyvinyl chloride will be made difficult, and as a result uniform dispersions cannot be attained.

On the other hand, if the rubber content is below 40% by weight, the improvement in the impact resistance is small, and it is disadvantageous economically, to impart the desired impact strength by the use of a large amount of copolymer. Moreover, the other physical properties, such as heat and temperature resistance and gas permeability, become deficient. That is, the compositional ratio by weight of the rubber component and the plastics component is preferably in the range of (40 to 75)/(60 to 25).

For the rubber component, a butadiene polymer or a butadiene/styrene copolymer which has or has not been cross-linked is used. It has been found that with butadiene/styrene copolymers, a styrene content of up to 40% by weight produces excellent results.

For the plastics component, a polymer produced by causing a monomer mixture of styrene and methyl methacrylate containing a cross-linking agent to be adsorbed and polymerized on rubber latex particles is used. It has been found that the styrene content in the monomer mixture is preferably in the range from 40 to 80% by weight.

In this case, the plastics component may be polymerized in one step on the rubber component. It has been found, however, that it is preferable to resort to a two-step polymerization process in which the plastics component is divided into two parts, and which comprises carrying out a first polymerization step, adding methyl methacrylate or a monomer mixture of styrene with methyl methacrylate as its principal constituent containing a cross-linking agent upon completion of the greater part of the first polymerization step, and carrying out a second polymerization step.

This method has the effect of further im-

proving the blending of the MBS resin produced with the polyvinyl chloride and increasing the rate of dispersion into the vinyl chloride.

The quantity of monomers polymerized in the second step is preferably 30% by weight or less of that in the first step. Furthermore, when the polymerization of the plastics component with the rubber component is carried out in two steps, it is possible to omit the addition of the cross-linking agent in either one of the first and second steps.

The cross-linking agent to be used according to the invention is selected from among those which copolymerize well with styrene, butadiene, and methyl methacrylate. Examples of suitable cross-linking agents are divinyl benzene and dimethacrylates such as mono-, di-, tri-, or tetra-ethylene glycol dimethacrylate and 1,3-butylene glycol dimethacrylate. The quantity of the cross-linking agent used is from 0.01 to 5% by weight of the total quantity of the monomers.

The polyvinyl chlorides suitable for use according to the invention are those obtainable by various known methods, such as emulsion, polymerization and suspension polymerization. In addition to homo-polymers, it is also possible to use a copolymer of at least 70% of vinyl chloride and other monomers to be copolymerized therewith, such as mono-olefine monomers, or mixtures thereof. From 5 to 20 parts by weight of a resin obtained according to the invention is mixed with from 95 to 80 percent by weight of vinyl chloride polymer.

While it is possible to carry out the mixing in general, with the materials in powder form by means of apparatus such as a roll mill or a Banbury type mixer, it is also possible to mix the latex obtained and the polyvinyl chloride latex, and then to subject the resulting mixture to salting out or spray drying to produce a mixed resin composition.

As described above, the MBS resins according to the invention, when mixed with polyvinyl chlorides, impart excellent transparency and impact resistance. The use of these MBS resins, however, is not limited to only that for mixing with polyvinyl chlorides, these MBS resins being useful also for mixing with other resins, for example, chlorinated polyvinyl chloride and polyvinylidene chloride copolymers so as to increase their strength and resistance impact.

The following Examples are set forth, in order to illustrate the present invention.

EXAMPLE 1

A 10 litre stainless-steel autoclave provided with an agitator was charged under a vacuum with a polymerization mixture comprising 1 g. of cumene hydroperoxide (CHP), 800g. of butadiene, 200 g. of styrene, and 5 g. of triethylene glycol dimethacrylate (DMA) and

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3,000 cc. of distilled water containing 10 g. of sodium bis-octyl sulphosuccinate, 0.05 g. of ethylenediamine tetraacetic acid disodium monohydrate, 0.5 g. of rongalite, 0.03 g. of ferrous sulphide, and 0.15 g. of sodium pyrophosphate. The materials thus charged were then allowed to react at 40°C for approximately 17 hours giving a butadiene-styrene latex, after which time no further pressure drop was observable.

Next, first monomer mixture of 300 g. of styrene containing 0.5 g. of CHP, 3 g. of DMA, 200 g. of methyl methacrylate, 0.3 g. of rongalite, and 1,500 cc. of distilled water were added to the resulting charge, and the resulting mixture was agitated at high speed for 30 minutes. Thereafter, the charge was heated to 60°C and allowed to react for 5 hours.

The latex thus obtained was cooled to 30°C and a second monomer mixture comprising 200 g. of methyl methacrylate containing 0.2 g. of CHP, 1.0 g. of DMA, 0.1 g. of rongalite, and 600 cc. of distilled water were further added to the charge, which was then agitated for 30 minutes. Thereafter, the charge was heated to 60°C and allowed to react for 5 hours.

The latex thus obtained was salted out at 50°C with a 1% by weight sodium chloride solution and filtered. The particles of copolymer containing 47.1% by weight of butadiene, 29.4% by weight of styrene and 23.5% by weight of methyl methacrylate that were filtered out were washed with water and then dried, giving an MBS resin with a η_{inh} value of 0.032 in a yield of 98.5%.

13 parts by weight of this resin were mixed with 87 parts by weight of a polyvinyl chloride of a polymerization degree of 800 containing 2 parts by weight of dibutyl tin dilaurate, and the resulting mixture was roll-mixed at 140°C for 4 minutes and then pressed at 180°C under pressure of 100 kg./cm.² into a sheet of 3-mm. thickness.

The Charpy impact strength of this sheet,

as tested on a notched test piece, was 85 kg.cm./cm². The light transmittance of the sheet according to Japan Industrial Standards Designation K 6714 was 81.5% and the haze value was 3.5%. Furthermore, when a sheet of 1-mm. thickness of the same resin was bent through 180°C almost no clouding was observable.

In addition, when a mixture of 0.1 part by weight of calcium stearate, 0.36 part by weight of zinc stearate, and 6 parts by weight of an epoxy compound of soybean oil was used in place of the above described stabilizing agent, and bottles, each of 530 cc. capacity and 25 g. weight were formed by means of an extruding machine, bottles of excellent transparency were obtained.

Fifty of these bottles were cooled to 50°C, filled with water, and subjected to repeated free drop tests from a height of 1 metre until breakage occurred. As a result, the average number of drops for breakage was 29 drops. For comparison, a similar test was carried out with similar bottles produced only from polyvinyl chloride, in which case the average result was 2 drops for breakage.

EXAMPLE 2

The process was set forth in Example 1 was followed except that the amount of cross-linking agent was changed.

In Sample A all the methyl methacrylate and cross-linking agent were copolymerized, with styrene, in the presence of the rubber component latex in a single polymerisation step. In Samples B, C, D and E, some of the methyl methacrylate were copolymerized with styrene and cross-linking agent in the presence of the rubber component latex in a first step, the remainder of the methyl methacrylate and cross-linking agent being copolymerized in a second step.

The compositions of the samples are set out in Table 1 below, and their properties are set out in Table 2.

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TABLE 1

Sample	Rubber Component			Plastics Component					
				First Polymerisation Step			Second Polymerisation Step		
Butadiene (parts) by weight	Styrene (parts) by weight	DMA (parts) by weight	Styrene (parts) by weight	Methyl methacrylate (parts) by weight	DMA (parts) by weight	Methyl methacrylate (parts) by weight	DMA (parts) by weight		
A	40	10	0.25	15	20	0.175	0	0	
B	40	10	0.25	15	10	0.850	10	0.3	
C	40	10	0.25	15	10	0.500	10	0.2	
D	40	10	0.25	15	10	0.30	10	0.1	
E	40	10	0.25	15	10	0.15	10	0.05	
Comparison F	40	10	0	20	10	0	10	0	

TABLE 2

Sample	η_{sp}/c	Increase in Impact resistance (%) [*]	Number of repeated drops (500 cc., 25 g. bottle)	Transparency %
A	0.045	13	20	79.0
B	0.013	15	19	83.5
C	0.020	13	22	83.2
D	0.025	12	25	82.2
E	0.032	11	29	81.5
Comparison F	0.116	10	8	61.5

* Charpy impact strength tests were carried out on notched test pieces of resins with varying mixture proportions, and the point of transition from brittle fracture to ductile fracture was taken in each case.

WHAT WE CLAIM IS:

1. A process for producing a butadiene-styrene-methyl methacrylate cross-linked copolymer in particulate form comprising from 5 24 to 60% by weight of butadiene, from 22 to 43% by weight of styrene, and from 5 to 46% by weight of methyl methacrylate, which comprises carrying out polymerisation of 10 styrene, methyl methacrylate and a cross-linking agent (the plastics component) in the presence of a latex of polybutadiene or a butadiene-styrene copolymer (the rubber component), the styrene and methyl methacrylate in the plastics component comprising from 60 15 to 25% by weight and the butadiene and styrene (if any) in the rubber component comprising from 40 to 75% by weight, based on the total weight of butadiene, styrene and methyl methacrylate, and the cross-linking 20 agent comprising from 0.01 to 5% by weight, based on the total weight of butadiene, styrene and methyl methacrylate.

2. A process as claimed in claim 1 wherein the styrene, methyl methacrylate and cross-linking agent are polymerised in the presence of the rubber component in two steps.

3. A process as claimed in claims 1 or 2, wherein the butadiene content in the rubber component is at least 60% by weight.

4. A process as claimed in any of claims 1 to 3 wherein the quantitative ratio of the styrene and methyl methacrylate subjected to polymerisation is 40 to 80% by weight to 60 to 20% by weight.

5. A process as claimed in any of claims 1 to 4 wherein the rubber component is cross-linked.

6. A process as claimed in claim 2 wherein, in a first polymerisation step, a first polymer-

isation mixture containing some or all of the styrene and some of the methyl methacrylate in the plastics component is polymerised with some of the cross-linking agent in the presence of the polybutadiene or butadiene-styrene copolymer latex, and, in a second 45 polymerisation step, initiated after the first polymerisation step is complete, a second polymerisation mixture comprising the remainder of the methyl methacrylate and the remaining styrene (if any) is polymerised with the remainder of the cross-linking agent in the presence of the resulting latex, the first polymerisation mixture comprising more than 70% by weight of the styrene and methyl methacrylate in the plastics component. 55

7. A process as claimed in claim 1 substantially as described with reference to either of the Examples.

8. Butadiene-styrene-methyl methacrylate cross-linked copolymers when produced by a process as claimed in any of the preceding claims. 60

9. A composition comprising a copolymer as claimed in claim 8 and polyvinyl chloride or a copolymer having vinyl chloride as its principal constituent by weight. 65

10. A composition as claimed in claim 9 comprising 5 to 20 parts by weight of butadiene styrene-methyl methacrylate copolymer and from 95 to 80 parts by weight of polyvinyl chloride or vinyl chloride copolymer. 70

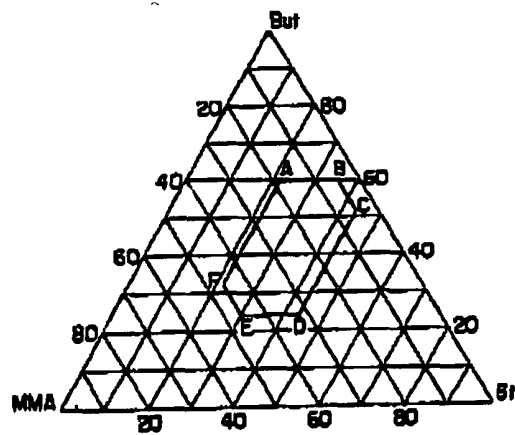
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